

OXIDATION STATE OF NAKHLITES AS INFERRED FROM FE-TI OXIDE EQUILIBRIA AND AUGITE/MELT EUROPIUM PARTITIONING. J. Makishima¹, G. McKay², L. Le³, M. Miyamoto¹ and T. Mikouchi¹. ¹Department of Earth and Planetary Science, Graduate school of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan, makki@eps.s.u-tokyo.ac.jp, ²Mail Code SR, NASA Johnson Space Center, Houston, TX 77058, USA, ³ESC Group, Jacobs Sverdrup, Houston, TX 77258, USA.

Introduction: Recent studies have shown that Martian magmas had wide range of oxygen fugacities (fO_2) and that this variation is correlated with the variation of La/Yb ratio and isotopic characteristics of the Martian basalts, shergottite meteorites [1,2]. The origin of this correlation must have important information about mantle sources and Martian evolution. In order to understand this correlation, it is necessary to know accurate value of oxidation state of other Martian meteorite groups. Nakhilites, cumulate clinopyroxenites, are another major group of Martian meteorites and have distinctly different trace element and isotopic characteristics from shergottites [3]. Thus, estimates of oxidation state of nakhilites will give us important insight into the mantle source in general.

Several workers have estimated oxidation state of nakhilites by using Fe-Ti oxide equilibrium [e.g. 4,5]. However, Fe-Ti oxides may not record the oxidation state of the parent melt of the nakhilite because it is a late-stage mineral. Furthermore, there is no comprehensive study which analyzed all nakhilite samples at the same time. Therefore, in this study (1) we reduced the uncertainty of the estimate using the same electron microprobe and the same standards under the same condition for Fe-Ti oxide in 6 nakhilites and (2) we also performed crystallization experiments to measure partition coefficients of Eu into pyroxene in the nakhilite system in order to estimate fO_2 when the pyroxene core formed (i.e. Eu oxybarometer [e.g. 2,6]).

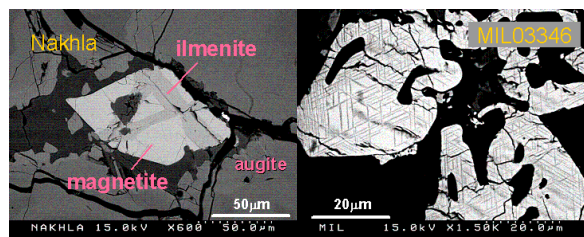


Fig. 1 BSE images of Fe-Ti oxides in Nakhla (left) and in MIL03346 (right). The bright areas are magnetite and light gray areas are ilmenite, which are surrounded by augite or mesostasis. We can clearly see wider ilmenite lamellae (~20 μ m across) in Nakhla compared to much thinner lamellae (< 1 μ m across) in MIL03346.

Method: Fe-Ti oxides (magnetite-ilmenite) in 6 nakhilites (MIL03346, NWA817, Y000593, Nakhla, Governador Valadares, NWA998) were measured. We calculated their fO_2 using two different geothermometer/oxygen models, Ghiorso and Sack [7] and the Ca-QUILF [8] models that differ in elements accounted for as well as in the solution models used.

We calibrated the Eu oxybarometer for the nakhilite using the synthetic NJ4 composition, which we believe is the closest to the Nakhla parent melt [9]. We doped this NJ4 composition with percent level REEs... Then, we put this starting material in the furnace at 1300 $^{\circ}$ C for 48 hours to homogenize it, quenched and put back below the liquidus (1150 ~ 1160 $^{\circ}$ C) and grew pyroxenes isothermally or during slow cooling. Runs were performed under the three oxygen fugacities between the Iron-Wustite (IW) buffer and the Quartz-Fayalite-Magnetite (QFM) buffer (~ 3.5 log units above IW). We analyzed the resulting samples with the JEOL JXA8900L electron microprobe at University of Tokyo by using well-characterized REE standards and calculated the D(Eu/Gd).

Table 1. Result of fO_2 estimates for the nakhilite by the Fe-Ti method

	T($^{\circ}$ C)	log fO_2 (atm)	log fO_2 (Δ QFM)
Ghiorso & Sack [7]			
MIL03346	n/a	n/a	n/a
NWA817	618 - 719	-16.92 to -20.61	0.03 to -0.72
Y000593	610 - 658	-19.69 to -21.34	-1.03 to -1.19
G.V.	655 - 692	-18.50 to -20.04	-0.84 to -1.29
Nakhla	648 - 720	-17.80 to -19.93	-0.89 to -1.09
NWA998	674 - 680	-18.21 to -18.71	-0.26 to -0.52
Ca-QUILF [8]			
MIL03346	n/a	n/a	n/a
NWA817	667 - 724	-16.46 to -18.54	-0.07 to -0.68
Y000593	650 - 680	-18.58 to -19.57	-1.00 to -1.14
G.V.	649 - 688	-18.20 to -19.85	-0.91 to -1.40
Nakhla	671 - 712	-17.70 to -18.81	-0.98 to -1.10
NWA998	682 - 700	-17.30 to -18.09	-0.27 to -0.58

Results and Discussion: Ilmenite lamellae in MIL03346 were too thin (<1 μ m) for analysis by microprobe (Fig. 1). The width of ilmenite lamellae in nakhilites studied is consistent with the cooling model proposed for the nakhilite igneous body [10]. We checked whether magnetite and ilmenite are in

equilibrium by using the Mg/Mn partitioning test from [11]. All Fe-Ti oxides we chose have cation sums within error of 3.00 and are therefore in stoichiometry. The fO_2 results by the Fe-Ti oxide method are summarized in Table 1. The absolute error on the fO_2 estimates is ± 0.5 log unit at most as reported in [12]. The estimated values are quite similar in both models. Although the fO_2 estimates for NWA817 and NWA998 are slightly higher than those for the other nakhlites, there is generally good agreement among the fO_2 estimates and equilibrated temperatures of the 5 nakhlites within error. This result suggests that Fe-Ti oxides in all 5 nakhlites were equilibrated at 650 ~ 700 °C under QFM-0.5 ~ QFM-1. This oxidation state is consistent with the previous estimates using Fe-Ti oxide equilibrium by several authors [e.g. 4,5].

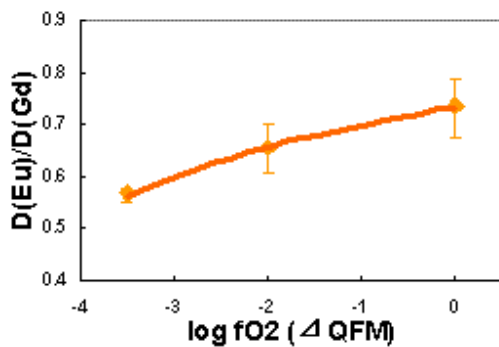


Fig. 2 Calibration of D(Eu)/D(Gd) in synthetic pyroxene versus oxygen fugacity (in log unit relative to QFM buffer).

Fig. 2 shows our calibration of D(Eu/Gd) in synthetic pyroxene vs. oxygen fugacity for our nakhlite experiments. This calibration curve has a similar trend to that for the shergottite calibration [13] and that predicted by theory [6]. Unlike the shergottite, the bulk composition of the nakhlite does not represent its parent melt composition. Thus, in order to calculate D(Eu)/D(Gd) of nakhlite melt, we used the partition coefficients of REE in the synthetic Nakhla augite/melt from the experimental study [14] as well as the published REE data of Nakhla augite core [15] and Nakhla whole rock [16]. Table 2 shows this calculated D(Eu)/D(Gd) value of Nakhla melt and our experimental D value under 3 oxygen fugacities. The fO_2 for Nakhla was estimated by comparing these two D values. Our study suggests that Nakhla augite crystallized at 1150~1160 °C under QFM-1 (± 1.0) buffer (Table 2 and Fig.2).

These two independent results show us that the magmatic oxidation state for the nakhlite did not change throughout their crystallization. This presents a contrast to the case of the shergottite, in which the fO_2 values using the Eu oxybarometer are systematically

lower by 1~2 log unit than those estimated from the Fe-Ti oxides [2,13]. The correlation between the whole rock La/Yb ratio and fO_2 seen in shergottites seems not to be applicable to the nakhlite group (Fig. 3), indicating that the nakhlite source had a very different evolutionary history than the mantle from which the shergottites were derived.

Table 2. Pyroxene D(Eu)/D(Gd)			
Expt	fO_2 (Δ QFM)	D(Px)	Nakhla melt
817	-3.5	0.57 ± 0.01	0.70 ± 0.04
818	-2.0	0.66 ± 0.01	
819	0	0.74 ± 0.01	

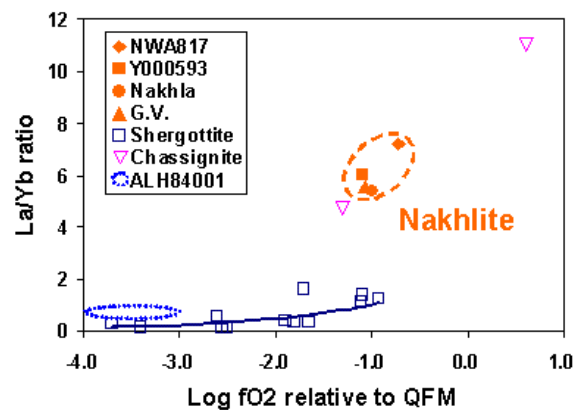


Fig. 3 Whole rock La/Yb ratio versus oxygen fugacity for the martian meteorites. The fO_2 data are from [1,17,18] and La/Yb data are from [3,17,19,20].

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